Chapter 14: Chemical Kinetics

Kahoot!

1. The rate of a reaction can be increased by: increasing reactant concentrations, increasing temperature, adding a suitable catalyst, all of the above
2. Over time, the rate of most chemical reactions tends to ___. Increase, decrease, remain constant, oscillate
3. Consider the reaction $A_3 + 3B_2 \rightarrow 3AB_2$. If A_3 consumption is -0.750 M/min, then B_2 consumption is: -0.750 M /min, -0.225 M /min, -0.250 M /min, -2.25 M /min
4. If tripling the concentration of reactant A multiplies the rate by a factor of 9, the reaction is ___ order in A. 0, 1, 2, 3
5. What are the correct units for k of a 5th order reaction? $M^{-2}\ s^{-1}$, $M^{-3}\ s^{-1}$, $M^{-4}\ s^{-1}$, $M^{-5}\ s^{-1}$
6. If Rate = k[A][B], what is the overall order of this reaction? 1, 2, 3, 4
7. If $W + X \rightarrow Y + Z$, Rate = k[W], what is the reaction order for X? 0, 1, 2, 3
8. Select the incorrect statement:
   - the orders are not taken from the coefficients in the balanced eqn
   - for a 1st-order reaction, a plot of ln[A] versus t is linear
   - for a 0th-order reaction, a plot of [A] versus t is parabolic
   - the overall order of a 0th order reaction is 0
9. The time required for the concentration of a reactant to be reduced by half is ___. Midpoint of the reaction, equivalence point of the reaction, half-rate of the reaction, half-life of the reaction
10. If a reaction is 1st order in [A], which of the following will yield a linear plot? [A] vs time, 1/[A] vs time, ln[A] vs time, $[A]^2$ vs time
11. If a reaction is 2nd order in [A] which of the following will yield a linear plot? [A] vs time, 1/[A] vs time, ln[A] vs time, $[A]^2$ vs time
12. If a reaction is 0th order in [A] which of the following will yield a linear plot? [A] vs time, 1/[A] vs time, ln[A] vs time, $[A]^2$ vs time
13. ___ is the minimum energy required for a collision between molecules to generate product. Initial energy, internal energy, external energy, energy of activation
14. The rate-determining step is the ___ step in a reaction mechanism. First, last, fastest, slowest
15. In a reaction mechanism, a species that is produced then consumed is ___. A byproduct, a catalyst, an intermediate, a reactant
16. What is the molecularity of $H_2 + NO \rightarrow N + H_2O$? unimolecular, bimolecular, trimolecular, termolecular
17. What is the rate law for elementary step $H_2 + NO \rightarrow N + H_2O$? rate=$k[H]^2[NO]$, rate=$k[H_2][NO]$, rate=$k[H_2][N][O]$, rate==$k[H]^2[NO] - [N][H_2O]$
18. In a reaction mechanism, a species that is consumed then produced is ___. A byproduct, a catalyst, an intermediate, a reactant
19. Adding a catalyst increases the rate of a reaction by: increasing molecular velocities, increasing molecular collisions, decreasing the energy of activation, all of the above

Whiteboard Examples

Experimental Determination Example: Determine the rate law, the rate constant and the reaction orders for each reactant and the overall reaction order using the data given below.

Experiment	$[A]_0$	$[B]_0$	Initial Rate M/s
1	0.100	0.100	4.0×10^{-5}
2	0.100	0.200	4.0×10^{-5}

3	0.200	0.100	16.0 x 10^{-5}

In other words we want to find, m, n, and k for rate = $k[A]^m[B]^n$

Comparison of 1 & 2 indicates that changes in [B] has no impact – let's prove it

$$\frac{rate_1}{rate_2} = \frac{k[A]_1^m[B]_1^n}{k[A]_2^m[B]_2^n}$$

$$\frac{4.0\times10^{-5}\,\frac{M}{s}}{4.0\times10^{-5}\,\frac{M}{s}} = \frac{k(0.100M)^m(0.100M)^n}{k(0.100M)^m(0.200M)^n}$$

$$1 = \left(\frac{1}{2}\right)^m \rightarrow n = 0 \text{ which means } rate = k[A]^m[B]^0 = rate = k[A]^m$$

Now we need to find m by picking two experiments in which [A] changes let's use 2 & 3

$$\frac{rate_2}{rate_3} = \frac{k[A]_2^m}{k[A]_3^m}$$

$$\frac{4.0\times10^{-5}\,\frac{M}{s}}{16.0\times10^{-5}\,\frac{M}{s}} = \frac{k(0.100M)^m}{k(0.200M)^m}$$

$$\frac{1}{4} = \left(\frac{1}{2}\right)^m \rightarrow n = 2 \text{ which means } rate = k[A]^2$$

Finally we can use any of the three trials to find our constant k and plug them into the rate law.

$$rate = k[A]^2$$

$$4.0\times10^{-5}\,\frac{M}{s} = k(0.100M)^2 \rightarrow k = \frac{4.0\times10^{-5}\,\frac{M}{s}}{0.0100M^2} = 4.0\times10^{-3}M^{-1}s^{-1}$$

Putting it all together we get a rate law of:

$$rate = 4.0\times10^{-3}M^{-1}s^{-1}[A]^2$$

Example for Fast Equilibrium Approximation: What is the rate law for the mechanism below?

$$step1: \quad NO + O_2 \xrightarrow{k_1} NO_3 \qquad (fast)$$
$$step2: \quad NO + NO_3 \xrightarrow{k_2} 2NO_2 \quad (slow)$$

-- *when a fast step preceeds the slow step we assume the fast step is in eq or reversible*

$$step\ 1: \quad NO + O_2 \underset{k_{-1}}{\overset{k_1}{\longleftrightarrow}} NO_3 \quad (fast)$$
$$step\ 2: \quad NO + NO_3 \xrightarrow{k_2} 2NO_2 \quad (slow)$$

-- we can then write the rate of step1 as rate $=k_1[NO][O_2] = k_{-1}[NO_3]$ solving for $[NO_3]$,

$$[NO_3] = \frac{k_1}{k_{-1}}[NO][O_2]$$

-- the rate for step2: rate = $k_2[NO][NO_3]$

we can plug in the relationship from step1 into this equation,

$$rate = k_2[NO]\frac{k_1}{k_{-1}}[NO][O_2] = k_2\frac{k_1}{k_{-1}}[NO]^2[O_2]$$

Applied Fast Equilibrium Example: The rate laws for the thermal and photochemical decomposition of NO_2 are different. Which of the following mechanisms are possible for thermal and photochemical rates given the information below?

Thermal rate = $k[NO_2]^2$

Photochemical rate = $k[NO_2]$

a.)

$$NO_2 \xrightarrow{slow} NO + O$$
$$O + NO_2 \xrightarrow{fast} NO + O_2$$

b.)

$$NO_2 + NO_2 \xrightarrow{fast} N_2O_4$$
$$N_2O_4 \xrightarrow{slow} NO + NO_3$$
$$NO_3 \xrightarrow{fast} NO + O_2$$

c.)

$$NO_2 + NO_2 \xrightarrow{slow} NO + NO_3$$
$$NO_3 \xrightarrow{fast} NO + O_2$$

a.) rate = $k[NO_2]$ which is consist with the photochemical rate

b.) fast step before slow so we assume eq:

$$NO_2 + NO_2 \underset{k_{-1}}{\overset{k_1}{\longleftrightarrow}} N_2O_4 \qquad k_1[NO_2]^2 = k_{-1}[N_2O_4] \rightarrow [N_2O_4] = \frac{k_1}{k_{-1}}[NO_2]^2$$

$$N_2O_4 \xrightarrow{k_2} NO + NO_3 \qquad rate = k_2[N_2O_4] = k_2\frac{k_1}{k_{-1}}[NO_2]^2$$

therefore this mechanism is consistent with the thermal rate

c.) rate = $k[NO_2]^2$ which is also consistent with the thermal rate

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